AR201 - 13055

PINE CHEMICALS ASSOCIATION

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May 23, 2001

Administrator
US EPA
P.O. Box 1473
Merrifield, VA 22116

Re: HPV Test Plans and Robust Summaries for Tall Oil and Related Substances and Tall Oil Fatty Acids and Related Substances

Dear Ms Whitman;
On behalf of the member companies of the Pine Chemicals Association's High Production Volume Chemical Task Force, I am pleased to submit the Test Plans and Robust Summaries for the chemical categories designated as;

"Tall Oil and Related Substances"

"Tall Oil Fatty Acids and Related Substances"

The submission includes one electronic copy of each in pdf format, and a hard copy which will be mailed to EPA Headquarters. The registration number for our Consortium is

Should you have any questions concerning our submission please feel free to contact me at (770) 209-7534 or at wjones@tappi.org.

Sincerely,

Walter L. Jones
President & COO

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MR 48236

HIGH PRODUCTION VOLUME (HPV) CHEMICAL CHALLENGE PROGRAM

TEST PLAN

for

TALL OIL
AND
RELATED SUBSTANCES

CAS No. 8002-26-4
CAS No. 8016-81-7
CAS No. 68140-I 6-9
CAS No. 68152-92-I
CAS No. 65997-01-5
CAS No. 68647-71-2
CAS No. 65997-02-6

Submitted to the US EPA

BY

The Pine Chemicals Association, Inc.
HPV Task Force
Consortium Registration #

Table of Contents

Test Plan For Tall Oil and Related Substances

Test Plan for Tall Oil and Related Substances

Summary

The Pine Chemicals Association, Inc. (PCA) is sponsoring 36 HPV chemicals. This Test Plan addresses the following seven chemicals, known collectively as Tall Oil and Related Substances:

8002-26-4, Tall Oil
8016-81-7, Tall Oil Pitch
68140-16-9, Tall Oil Pitch, sodium salt
68152-92-1, Tall Oil, disproportionated
65997-01-5, Tall Oil, sodium salt
68647-71-2, Tall Oil, potassium salt
65997-02-6, Wastewater, tall oil soap acidulation

These seven substances are all derived from or closely related to tall oil, a by-product from the pulping of pine trees. Tall oil and the various derivatives in this group are all complex mixtures (Class 2 substances). They are composed of numerous chemicals -- the most common of which are rosin and fatty acids, with lesser amounts of terpenes and sterols. Each species of pine tree yields a somewhat different mix of tall oil, and even within a species, the composition of the tall oil could be influenced by the climate and local terrain. However, all the members of this group are similar in chemical composition, being predominantly the extractives that remain after the pulping of wood. Thus, PCA has elected to treat these chemicals as a category for purposes of the HPV program.

Where applicable, PCA will conduct physical/chemical property and environmental fate testing on these substances. Available data show tall oil is non-toxic in acute studies. PCA will conduct testing for the other SIDS health effects endpoints. A representative of the category will be used for ecotoxicity, *in vitro* genotoxicity, and mammalian toxicity testing.

Tall oil is the source of most of the substances in this category, except acidulation wastewater (which is essentially wastewater containing about 1 - 2 % tall oil). Tall oil is used as the feedstock for fractional distillation, from which a variety of useful fractions (rosin, fatty acids, distilled tall oil, heads and pitch) are derived.

Tall oil pitch (the residue after other fractions are distilled away) is primarily consumed as fuel by the tall oil processor; small amounts are converted to salts for use in the asphalt industry. Tall oil salts are used in the production of soaps and detergents, and in metal working fluids. Disproportionated tall oil is used in the rubber industry as a processing aid.

Tall oil (CAS# 8002-26-4) has been selected as the representative substance in this group for testing for the SIDS data. PCA has reviewed existing data on tall oil and determined that other than acute toxicity, there are no other data on the SIDS endpoints. The available data demonstrate that tall oil is non-toxic following acute oral exposure. Because there are no data on ecotoxicity, repeat dose toxicity, *in vitro* genotoxicity, reproductive or developmental toxicity, tall oil will be tested to fulfill these endpoints. A brief summary of the available data for the substances in this category, and the anticipated additional testing, is described below and in Table 1.

Table 1
Matrix of Available Adequate Data and Proposed Testing
On Tall Oil and Related Substances*

	Required SIDS Endpoints										
Chemical and CAS #	**Partition Coef.**	**Water Sol.**	**Biodeg.**	**Acute Fish**	**Acute Daph.**	**Acute Algae**	**Acute oral**	**Repeat Dose**	**In vitro genetox (bact.)**	**In vitro genetox (non-bact)**	Repro/ Develop
8002-26-4, Tall Oil	Test	Test	Adeq.	Test	Test	Test	Adeq.	Test	Test	Test	Test/ Test
8016-81-7, Tall Oil Pitch	Test	LM	Adeq.	C	C	C	C	C	C	C	C
68140-I 6-9, Tall Oil Pitch, sodium salt	Test	Test	Test	C	C	C	C	C	C	C	C
68152-92-1, Tall Oil, dispro-portionated	Test	Test	Test	C	C	C	C	C	C	C	C
65997-01-5, Tall Oil, sodium salt	Test	Test	Test	C	C	C	C	C	C	C	C
68647-71-2, Tall Oil, potassium salt	Test	Test	Test	C	C	C	C	C	C	C	C
65997-02-6, Wastewater, tall oil soap acidulation	No test	No test	No test	C	C	C	C	C	C	C	C

Adeq. Indicates adequate existing data
Test Indicates proposed testing
No test See test plan for explanation
LM Lack of a suitable analytical method precludes testing
C Indicates category read-down from existing or proposed test data on tall oil.
*No testing will be conducted for melting point, boiling point, vapor pressure, hydrolysis, photodegradation and transport and distribution between environmental compartments, as explained in the test plan.

Physical/Chemical Properties

Physical and chemical properties will be determined when appropriate; however, many of the physical and chemical properties are either inappropriate or cannot be measured for these compounds:

- The melting point will not be determined because these substances will not give a sharp melting point.
- Boiling points cannot be determined because these substances will decompose before they boil.
- Under ambient conditions, the vapor pressure of these chemicals is essentially zero and experimental measurement is not possible.
- The partition coefficients will be tested for six of the substances in this category. Partition coefficient testing can yield a range of values representing the various components, rather than a single value representing the mixture.
- The water solubilitv of five of the compounds in this grouping category will be determined.

Environmental Fate

With respect to the SIDS environmental fate endpoints:

- Determination of photodeqradation is not relevant, since the vapor pressure of these compounds at ambient temperature is essentially zero and they could not enter the atmosphere.
- Hydrolysis in water will not be determined for any of the compounds in this category because the members of this category have low water solubility and lack a functional group that would be susceptible to hydrolysis.
- Biodeqradation data will be generated for four of the compounds for which data are not already available.
- Transport and distribution between environmental compartments will not be determined due to the inability to provide usable inputs to the required model.

Ecotoxicity

- Existing **ecotoxicity** data are not reliable due to inconsistencies in, or artificial methods of, sample preparation. Consequently, tall oil will be retested for acute toxicity to fish, daphnia and algae under conditions that maximize the solubility, but reduce exposure to insoluble fractions that may cause nonspecific toxicological effects.

Mammalian Toxicity

- For the SIDS human health endpoints, there are sufficient data on acute toxicity for tall oil demonstrating that this compound is non-toxic. Data will be generated for tall oil for repeat dose toxicity, reproductive and developmental toxicity using OECD 422, as well as ***in vitro*** qenotoxicity testing.

The Pine Chemicals Association, Inc. HPV Task Force includes the following companies:

Akzo Nobel Resins
Akzo Nobel - Eka Chemicals Incorporated
Arizona Chemical Company
Asphalt Emulsion Manufacturers Association
Boise Cascade Corporation
Cognis Corporation
Eastman Chemical Co. (including the former Hercules Inc. Resins Division)
Georgia-Pacific Resins Inc.
ICI Americas (including the former Uniqema)
Inland Paperboard & Packaging, Inc.
International Paper Co. (including the former Champion International Corporation)
Koch Materials Co.
McConnaughay Technologies, Inc.
Mead Corp.
Packaging Corporation of America
Plasmine Technology, Inc.
Raisio Chemicals
Rayonier
Riverwood International
Smurfit - Stone Container Corporation
Westvaco
Weyerhaeuser Co.

The Task Force will be filing multiple test plans covering various chemicals. Not all members of the Task Force produce the substances covered by this test plan.

I. Description of Tall Oil and Related Substances

The Pine Chemicals Association, Inc. (PCA) is sponsoring seven HPV chemicals known collectively as Tall Oil and Related Substances. This group of chemicals consists of the following:

8002-26-4, Tall Oil
8016-81-7, Tall Oil Pitch
68140-I 6-9, Tall Oil Pitch, sodium salt
68152-92-1, Tall Oil, disproportionated
65997-01-5, Tall Oil, sodium salt
68647-71-2, Tall Oil, potassium salt
65997-02-6, Wastewater, tall oil soap acidulation

This group of chemicals are all closely related to tall oil, which is a by-product from the alkaline pulping of wood, especially pinewood. The precursors of tall oil in the tree are the so-called extractives that make up about 1% of the weight of the wood. These extractives are composed of numerous chemicals, the most common of which are rosin and fatty acids, with lesser amounts of terpenes and sterols. The extractives dissolve in the pulping liquor and are recovered from the liquor when it is concentrated and skimmed. The skimmed material is called tall oil soap and is the sodium salt of tall oil (CAS# 65997-01-5).

Tall oil soap is then acidulated with sulfuric acid to yield crude tall oil (CAS# 8002-26-4). A by-product of this acidulation is “wastewater, tall oil soap acidulation” (CAS# 65997-02-6), which is essentially a solution of sodium sulfate containing dilute amounts of tall oil. Commercially, crude tall oil is fractionally distilled to manufacture tall oil fatty acids and tall oil rosin. These important substances are the key members in other categories of HPV chemicals being sponsored by the Pine Chemicals Association, Inc. An intermediate fraction from the distillation process is distilled tall oil, which has the same CAS registry number as crude tall oil.

The other members of this HPV category are all closely related to tall oil. Disproportionated tall oil (CAS# 68152-92-1) is tall oil that has been stabilized to oxidation. Tall oil pitch (CAS# 8016-81-7) is the residue remaining when the tall oil fatty acids and the tall oil rosin have been distilled away. Its main use is for its fuel value. Zinkel and Russell (1989) noted that use of a material similar to tall oil pitch dates back to biblical times. In Genesis 6:14, Noah was instructed to *"pitch the ark within and without,"* indicating the historical use of pine tree resins, The remaining members of the group are simple salts of either tall oil or pitch.

As complex mixtures, tall oil and its derivatives are all considered Class 2 substances. Information on their composition, uses and the challenges of chemical analysis of these complex mixtures is described below.

A. Composition

All the members of this category are chemically complex, with their composition dependent on the source of the trees from which they were derived and the conditions under which the tall oil was distilled. They are all Class 2 substances. Consequently, they are not described in terms of their chemical composition, but only in general terms such as their acid number or their overall fatty acid or resin acid content (Zinkel and Russell 1989). However, some general information on the typical composition of each of the seven substances in this category is provided below.

1. Tall Oil (CAS# 8002-26-4)

The TSCA Inventory describes tall oil as, *"A complex combination of tall oil rosin and fatty acids derived from acidulation of crude tall oil soap and including that which is further refined. Contains at least 70% rosin. "* The two chief types of tall oil covered by this description are crude tall oil and distilled tall oil. The composition of a typical crude tall oil produced in the southeastern U.S. and a typical distilled tall oil are given in Table 2.

Table 2

Composition of Typical Tall Oils

	Crude Tall Oil	Distilled Tall Oil
Acid number	165	185
Fatty acids (%)	52	65
Resin acids (%)	40	30
Unsaponifiable matter (%)	8	5

The actual composition of both types of tall oil can vary widely. The composition of crude tall oil depends on the species of tree from which it was derived, while the composition of distilled tall oil depends upon the species of tree as well as the processing conditions under which it was manufactured. More detailed information on the composition of the tall oil to be tested for the HPV endpoints is provided in Table 3. The structures of some representative resin acids are shown in Figure 1.

Table 3
Comoosition of Distilled Tall Oil To Be Tested

Palmitic acid	$CH_3(CH_2)_{14}COOH$	3%
Palmitoleic acid"	$CH_3(CH_2)_XCH{=}CH(CH_2)_YCOOH$	1%
Stearic acid	$CH_3(CH_2)_{16}COOH$	1%
Oleic acid	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	28%
Linoleic acid	$CH_3(CH_2)_4CH{=}CH\text{-}CH_2CH{=}CH(CH_2)_7COOH$	19%
Linoleic acid, conjugated[b]	$CH_3(CH_2)_XCH{=}CHCH{=}CH\text{-}(CH_2)_YCOOH$	9%
Other fatty acids[c]		7%
Isopimaric acid		3%
Abietic acid		10%
Dehydroabietic acid		5%
Other resin acids		11%

a: x+y= 12
b: x usually 4 or 5; y usually 7 or 8; but x + y = 12
c: 5,9,12-octadecatrienoic acid; linolenic acid; 5,11,14-eicosatrenoic acid; cis,cis-5,9-octadecadienoic acid; eicosadienoic acid: elaidic acid; cis-1 1 octadecanoic acid; C-20, C-22, C-24 saturated acids.

2. Tall Oil Pitch (CAS# 8016- 81-7)

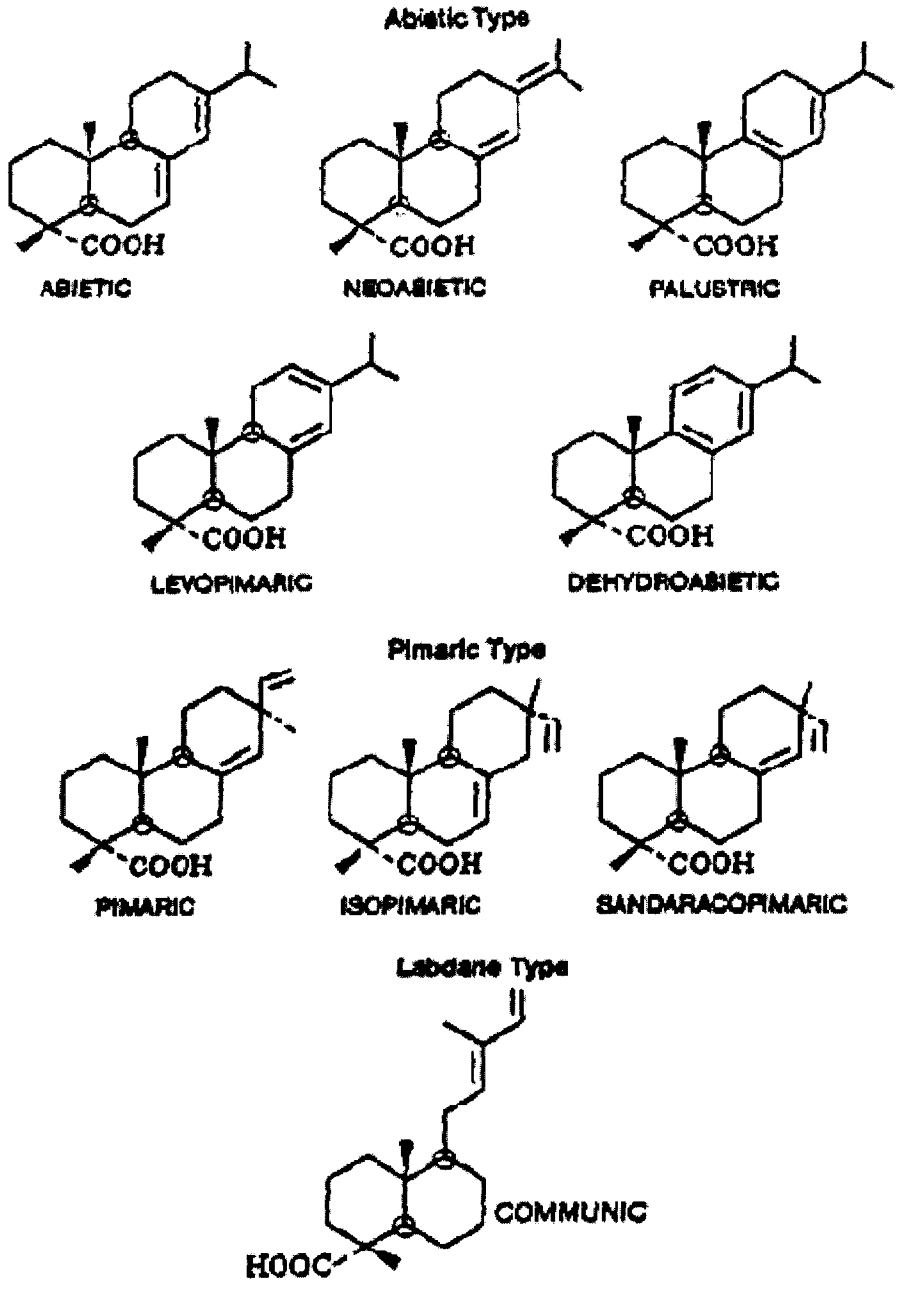
Tall oil pitch is a tarry semi-solid material with a composition very dependent on the processing conditions under which it was produced. As a consequence of its low acid number, its complex composition and its physical form, most of the pitch produced is consumed for its fuel value.

The TSCA Inventory defines tall oil pitch as ***"the residue from the distillation of tall oil. It contains primarily high boiling esters of fatty acids and rosin. It may also contain neutral materials, free fatty acids and resin acids".*** Pitch is primarily made up of high boiling, high molecular weight compounds formed at the high temperatures encountered during the fractionation process. These compounds include the esters of fatty acids and rosin, and small amounts of dimers and trimers of resin acids and fatty acids. Because pitch has such an extremely complex and variable composition, chemical analysis is not possible, and no typical composition can be presented.

3. Tall Oil Pitch, Sodium Salt (CAS# 68140- 16-9)

This substance is made by neutralizing tall oil pitch with sodium hydroxide. It is sold as an aqueous dispersion.

Figure 1



Common Resin Acids

Figure 1 shows the structures of some representative resin acids found in distilled tall oil and its derivatives.

4. Tall Oil, Disproportionated (CAS# 68152-92-I)

Disproportionated tall oil is distilled tall oil that has been heated with a catalyst that removes conjugated double bonds. The fatty acid and resin acid contents of the treated product are the same as the starting distilled tall oil (see Table 2), but some of the individual components are changed. For example, abietic acid is converted to dehydroabietic acid and linoleic acid is converted to oleic acid.

5. Tall Oil, Sodium Salt (CAS # 65997-01-5) and Potassium Salt (CAS # 68647-71-2)

The sodium salt of crude tall oil is also known as tall oil soap, the precursor to tall oil. Both the sodium and potassium salts of tall oil are also produced from distilled tall oil. The salts are made by treating tall oil with the appropriate base and dispersing the salt formed in water. These compounds, as the salts of a strong base and a weak acid, result in alkaline dispersions with the pH dependent on the salt concentration in the dispersion.

6. Wastewater, Tall Oil Soap Acidulation (CAS # 65997-02-6)

The TSCA Inventory defines this byproduct as, *"The aqueous layer formed by acidulation of tall oil soap with sulfuric acid during the production of tall oil. Composed primarily of a solution of sodium sulfate, the remainder being lignin and tall oil. "* Typically, tall oil soap acidulation wastewater is about a 12% solution of sodium sulfate, containing about 1 to 2% tall oil. This material has no commercial value except as a minor source of sodium for a kraft pulp mill. When that outlet is not available, the wastewater is typically discharged into a mill's wastewater treatment system.

No testing is planned for this material. The Pine Chemicals Association, Inc. (PCA) and the American Forest & Paper Association (AF&PA) petitioned the EPA to remove this byproduct from the HPV list on the grounds that it is an inorganic byproduct and should not be on the list, EPA suggested instead that this material should be treated as "dilute tall oil" since it contains some minor amount of tall oil and did not require independent testing.

B. Commercial Uses of Tall Oil and Related Substances

Tall oil is by far the most important member of this category from a commercial standpoint. The main use of tall oil is as a feedstock to the fractionation process, where tall oil is separated into its various fractions (rosin, fatty acids, distilled tall oil, heads, pitch).

Tall oil pitch, a tarry substance, is mainly consumed as fuel by the tall oil processor.

Tall oil pitch, sodium salt is used in the asphalt industry as a bonding agent in paving applications, or as a plasticizer in asphalt coatings.

Tall oil, disproportionated is important in the copolymerization of styrene and butadiene to produce rubber (SBR) and it is also used in the production of neoprene.

Tall oil, sodium and potassium salts are used in the production of soaps and detergents, as well as in metalworking fluids and lubricants.

Tall oil soap acidulation wastewater is composed of dilute tall oil and is of no commercial value. It is either recycled to the pulping process for the relatively small sodium value or is routed to the producer's wastewater treatment system.

C. Complexity of Analytical Methodology

All of the substances in this category are Class 2 substances. This, combined with the fact that tall oil is essentially insoluble in water and decomposes on heating at high temperature, creates a variety of analytical issues. Gas chromatography of methylated derivatives is the accepted method for the analysis of the members of this category. However, the solubility of tall oil is very low (about 10 ppm). PCA has verified the reliability of the standard analytical methods at such low concentrations. Based on the method validation work to date, it appears that the analytical procedures for tall oil and the remaining substances in this group (with the exception of pitch) will be adequate for the proposed testing. In spite of intensive efforts to develop an analytical method for pitch, analysis has proved to be impossible due to the complexity of this material.

II. Rationale for Selection of Representative Compound for Testing

Tall oil (CAS# 8002-26-4) (which includes crude and distilled tall oil) has been chosen as the representative of this category for testing purposes because it is commercially the most important member of the category. It is the commercial source of most of the substances in this category and the others are associated with its production. In addition, tall oil is the source of almost all of the 36 substances included in the entire PCA HPV program.

All the substances in this category are similar in chemical composition, being predominantly tall oil or its salts. Distilled tall oil will be used as the representative substance in this group for testing for the applicable SIDS ecotoxicity and mammalian toxicity tests. Distilled tall oil is more uniform in composition and physical state than crude tall oil. In addition, products based on distilled tall oil are far more common than those based on crude tall oil, which is used almost exclusively as a distillation feed.

Another criterion listed by EPA for grouping chemicals into a category is the use of the "family approach" of examining related chemicals when they are acids or acid salts, Although the salts of tall oil and tall oil pitch have different physical characteristics, they are included in this group because they are quickly converted into the free tall oil or tall oil pitch when they are treated by acid or by dilution, as they would be under typical toxicity testing conditions.

In summary, this category of chemicals fits the requirements of the EPA's HPV Challenge program for a chemical category, and tall oil is the most appropriate representative test material from this category.

III. Review of Existing Data and Development of Test Plan

PCA has undertaken a comprehensive evaluation of all relevant data on the SIDS endpoints of concern for the chemicals in this category. Other than acute toxicity, there are no other data on the HPV SIDS endpoints for this category. The availability of the data on the specific SIDS endpoints is summarized in Table 4 (identical to Table 1). Table 4 also shows where data will be generated.

Table 4
Matrix of Available Adequate Data and Proposed Testing On Tall Oil and Related Substances*

Chemical and CAS #	Required SIDS Endpoints										
	Partition Coef.	Water Sol.	Biodeg.	Acute Fish	Acute Daph.	Acute Algae	Acute oral	Repeat Dose	In vitro genetox (bact.)	In vitro genetox (non-bact)	Repro/ develop
8002-26-4, Tall Oil	Test	Test	Adeq.	Test	Test	Test	Adeq.	Test	Test	Test	Test/ Test
8016-81-7, Tall Oil Pitch	Test	LM	Adeq.	C	C	C	C	C	C	C	C
68140-16-9, Tall Oil Pitch, sodium salt	Test	Test	Test	C	C	C	C	C	C	C	C
68152-92-1, Tall Oil, dispro-portionated	Test	Test	Test	C	C	C	C	C	C	C	C
65997-01-5, Tall Oil, sodium salt	Test	Test	Test	C	C	C	C	C	C	C	C
68647-71-2, Tall Oil, potassium salt	Test	Test	Test	C	C	C	C	C	C	C	C
65997-02-6, Wastewater, tall oil soap acidulation	No test	No test	No test	C	C	C	C	C	C	C	C

Adeq. Indicates adequate existing data
Test Indicates proposed testing
No **test** See test plan for explanation
LM Lack of a suitable analytical method precludes testing
C Indicates category read-down from existing or proposed test data on tall oil.
*No testing will be conducted for melting point, boiling point, vapor pressure, hydrolysis, photodegradation, and transport and distribution between environmental compartments as explained in the test plan.

A. Evaluation of Existing Physicochemical Data and Proposed Testing

The basic physicochemical data required in the SIDS battery includes melting point, boiling point, vapor pressure, partition coefficient (K_{ow}), and water solubility.

Class 2 substances are composed of a complex mixture of substances and are often difficult to characterize. As noted above, tall oil, tall oil pitch, disproportionated tall oil and their various salts are Class 2 substances. Their composition is variable and cannot be represented by a definite chemical structural diagram. Due to this "complex mixture" characteristic of tall oil and related compounds, some physical property measurements, such as the partition coefficient are of questionable value because the methodology used to determine these properties will actually fractionate or partition the substances into various components. Since the methodology will alter the actual sample composition, the results of these tests are likely to be erroneous, difficult to interpret or meaningless.

1. Melting Point

Tall oil and the other non-salts in this grouping category are liquids at room temperature; tall oil pitch is a semi-solid. A sharp melting point cannot be obtained for any of these compounds due to the complex nature of these substances. The salts are solids under ambient conditions and heating them to determine the melting point would cause thermal decomposition.

2. Boiling Point

All of the non-salt members of this category are produced by high temperature, high vacuum distillation and are non-volatile at ambient temperatures. A boiling point at ambient pressure has no significance because when heated **to** high temperatures these materials will thermally decompose before they boil. The two salts in this category are solids. When heated to high temperatures, they will also thermally decompose before boiling. Accordingly, measurement of this property is inappropriate for all the substances in this category.

3. Vapor Pressure

Vapor pressures for tall oil and the other chemicals in this category at ambient temperatures are effectively zero, and their experimental measurement is inappropriate. The salt members of the category are solids and thus have no vapor pressure, so this end point cannot be measured. When dissolved in water, their solutions will reflect the vapor pressure of the water rather than the salt, and therefore measurement of this property is inappropriate.

4. Water Solubility

The water solubility of five compounds in this category will be determined using OECD protocol (105). The lack of a suitable analytical method for tall oil pitch precludes the determination of the water solubility.

5. Partition Coefficient

The partition coefficient (i.e., K,,) for six compounds in this category will be determined. Adequate data exist for tall oil and pitch although both will be retested with the other compounds in this category. Because all of these substances are Class 2 mixtures, the procedure (OECD 107) to determine the K_{ow} often yields a number of separate K_{ow} values rather than a single value representative of the mixture. Thus, the results will represent the partition coefficients of the components rather than the mixture.

Summary of Physicochemical Properties Testing: The water solubility of tall oil, disproportionated tall oil and two of the salts will be determined. The partition coefficients for six members of this category will be determined. Adequate data exist for tall oil and pitch although both will be retested with the other compounds in this category. Tests for the melting point, boiling point and vapor pressure are inappropriate.

B. Evaluation of Existing Environmental Fate Data and Proposed Testing

The fate or behavior of a chemical in the environment is determined by the rates or half-lives for the most important transformation (degradation) processes. The basic environmental fate data covered by the HPV Program includes biodegradation, stability in water (hydrolysis as a function of pH), photodegradation and transport and distribution between environmental compartments.

1. Biodegradation

Biodegradability provides a measure for the potential of compounds to be degraded by microorganisms. Depending on the nature of the test material, several standard test methods are available to assess potential biodegradability.

Of the chemicals in this category, two (tall oil and tall oil pitch) have existing data on the biodegradation endpoint. Biodegradation for disproportionated tall oil and the three salts will be determined.

2. Hydrolysis

Hydrolysis as a function of pH is used to assess the stability of a substance in water. Hydrolysis is a reaction in which a water molecule (or hydroxide ion) substitutes for another atom or group of atoms present in an organic molecule. If there is no group suitable to be displaced, then the organic compound is considered to be resistant to hydrolysis. None of the substances in the tall oil category contains an organic functional group that might be susceptible to this physical degradative mechanism. Therefore, hydrolysis need not be measured.

In addition, low water solubility often limits the ability to determine hydrolysis as a function of pH. All of the tall oil compounds have very low solubility in water. Therefore, these materials are expected to be stable in water and it would be unnecessary to attempt to measure the products of hydrolysis. With respect to the various tall oil salts, since they exist in an aqueous medium they hydrolyze (ionize) immediately, but form stable species. Consequently, it would also be unnecessary to measure this endpoint for tall oil salts.

3. Photodegradation

Due to their low water solubility and lack of any vapor pressure at ambient temperatures, there is no opportunity for any of these chemicals to enter the atmosphere. Thus, photodegradation is irrelevant. In addition, based on the constituents in these.complex mixtures, there is no reason to suspect that they would be subject to breakdown by a photodegradative mechanism. Consequently, this endpoint will not be determined for any of the substances in this category.

4. Transport and Distribution Between Environmental Compartments

The transport and distribution between environmental compartments is intended to determine the ability of a chemical to move or partition in the environment. The determination of this property requires the use of various models (e.g., level III model from the Canadian Environment Modeling Centre at Trent University). For Class 2 substances such as tall oil and related compounds, the required inputs to the model are either not available or impossible to determine including molecular mass, reaction half-life estimates for air, water, soil, sediment, aerosols, suspended sediment, and aquatic biota. In addition, while the partition coefficient is also required and can be determined, the multiple K_{ow} values typically derived for these substances (e.g., eight K_{ow} values for tall oil) are a consequence of sample fractionation and reflect various components in the mixture and are not representative of the mixture itself. Consequently, due to the inability to provide usable inputs to the required model, no determination of transportation and distribution between environmental compartments will be undertaken for tall oil and related compounds.

Summary of Environmental Fate Testing: Biodegradation data will be generated for four compounds in this category for which data are not already available. Photodegradation, hydrolysis and transport and distribution between environmental compartments are not applicable to these chemicals.

C. Evaluation of Existing Ecotoxicity Data and Proposed Testing

The basic ecotoxicity data that are part of the HPV Program include acute toxicity to fish, daphnia and algae. While there are existing data on these endpoints for some of the substances in this category, these data are conflicting and it is impossible to determine which, if any, of these findings are representative of ecotoxicity. The inconsistencies in how water samples were prepared for testing these endpoints render these data inadequate. Consequently, acute toxicity to fish, daphnia and alga will be retested for tall oil under conditions that maximize the solubility under the specific test exposure conditions, but reduce exposure to insoluble fractions that may cause nonspecific toxicological effects. In addition, the effect of both filtering to further minimize nonspecific physical effects, and of reducing the pH to the lower end of the acceptable range for test organism survival, will also be investigated for changes in toxicological effects. The results of preliminary tests will be used to select the most appropriate test conditions for the definitive test for each species.

Summary of Ecotoxicity Testing: The acute toxicity of tall oil to fish, daphnia and algae will be tested under conditions that maximize the solubility of the test material, but reduce exposure to insoluble fractions that may cause nonspecific toxicological effects.

D. Evaluation of Existing Human Health Effects Data and Proposed Testing

1. Acute Oral Toxicity

Acute oral toxicity studies investigate the effect(s) of a single exposure to a relatively high dose of a substance. This test is conducted by administering the test material to animals (typically rats or mice) in a single gavage dose. Harmonized EPA testing guidelines (August 1998) set the limit dose for acute oral toxicity studies at 2000 mg/kg body weight. If less than 50 percent mortality is observed at the limit dose, no further testing is needed. A test substance that shows no effects at the limit dose is considered essentially nontoxic. If compound-related mortality is observed, then further testing may be necessary.

Summary of Available Acute Oral Toxicity Data

Tall oil **is** non-toxic following acute oral exposure. The acute oral toxicity of tall oil has been determined in two studies in rats. The acute oral LD_{50} was > 5000 mg/kg in one study and > 6000 mg/kg in another study.

Summary of Acute Oral Toxicity Testing: Tall oil has been tested for acute oral toxicity and found to be non-toxic (i.e., LD_{50} > 5000 mg/kg) well above the guideline of 2000 mg/kg. Consequently, additional testing for this endpoint is not necessary.

2. Repeat Dose Toxicity

Subchronic repeated dose toxicity studies are designed to evaluate the effect(s) of repeated exposure to a chemical over a significant period of the life span of an animal. Typically, the exposure regimen in a subchronic study involves daily exposure (at least 5 consecutive days per week) for a period of not less than 28 days or up to 90 days (i.e., 4 to 13 weeks). The HPV program calls for a repeat dose test of at least 28 days. The dose levels evaluated are lower than the relatively high limit doses used in acute toxicity (i.e., LD_{50}) studies, but still substantially higher than potential human exposure levels. In general, repeat dose studies are designed to assess systemic toxicity, but the study protocol can be modified to incorporate evaluation of potential adverse reproductive and/or developmental effects,

Summary of Available Repeat Dose Toxicity Data

Tall oil will be tested for repeat dose toxicity. The test will be combined with the test for toxicity to reproduction and developmental toxicity in OECD *(422) Combined Repeated Dose Toxicity Study with the Reproduction/Developmental Toxicity Screening Test.*

Summary of Repeat Dose Toxicity Testing: Tall oil will be tested for repeated dose toxicity in conjunction with the reproduction/developmental toxicity screening test (OECD 422).

3. Genotoxicity - In vitro

Genetic testing is conducted to determine the effects of substances on genetic material (i.e., DNA and chromosomes). The gene, which is composed of DNA, is the simplest functional genetic unit. Mutations can occur spontaneously or as a consequence of exposure to chemicals or radiation. Genetic mutations are commonly measured in bacterial and mammalian cells, and the HPV program calls for both types of tests.

Summary of Available Genotoxicity Data

There are no existing data for tall oil for either the bacterial genotoxicity test or the mammalian genotoxicity test. Consequently, tall oil will be tested for both of these endpoints.

Summary of Genotoxicity Testing: Tall oil will be tested for genotoxicity in bacteria (OECD 471) and in vitro in mammalian cells (OECD 473).

4. Reproductive and Developmental Toxicity

Reproductive toxicity includes any adverse effect on fertility and reproduction, including effects on gonadal function, mating behavior, conception, and parturition.

Developmental toxicity is any adverse effect induced during the period of fetal development, including structural abnormalities, altered growth and post-partum development of the offspring.

The "toxicity to reproduction" aspect of the HPV Challenge Program can be met by conducting a reproductive/developmental toxicity screening test or adding a reproductive/developmental toxicity screening test to the repeated dose study (OECD 421 or OECD 422, respectively).

Summary of Reproductive/Developmental Toxicity Data

There are no existing data on tall oil that satisfy this endpoint. Consequently, tall oil will be tested for reproductive/developmental toxicity in conjunction with a repeat dose study using OECD 422.

Summary of Reproductive/Developmental Testing: Tall oil will be tested for reproductive/developmental toxicity in conjunction with a repeat dose study using OECD 422.

References

EPA. 2000. Data Collection and Development on High Production Volume (HPV) Chemicals. Fed. Reg. Dec. 26, Vol. 65(248): pp. 81686-81698.

Zinkel, D.F. and Russell, J., Eds. 1989. Naval Stores. Production, Chemistry, Utilization. Pulp Chemicals Association, New York.

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IV. Robust Summaries of Existing Data

PHYSICO-CHEMICAL PROPERTY – OCTANOL/WATER PARTITION COEFFICIENT	
Test Substance	
Chemical Name	Tall oil
CAS #	8002-26-4
Remarks	This substance is referred to as tall oil in the test plan for tall oil and related substances.
Method	
Method/Guideline followed	Testing was conducted according to OECD Test Method 117, "Partition Coefficient (n-Octanol/Water) High Performance Liquid Chromatograph (HPLC) Method"
Test Type	Partition coefficient
GLP (Y/N)	Y
Year (Study Performed)	1993
Test conditions	Tall oil was dissolved in methanol and the solution was analyzed by HPLC with UV detection using a mobile phase of methanol:buffer (3:1) at pH 2 and pH 7.5. As a reference substance, a mixture of seven materials was used.
Results	At pH 2, the log P_{ow} [K_{ow}] values of eight components in tall oil were 6.1, 6.5, 7.0, 7.4, 7.6, 7.8, 8.1, and 8.2. At pH 7.5, the log K_{ow} values of five components in tall oil were 3.5, 4.2, 4.5, 4.7, and 5.4.
Data Quality	Reliable without restrictions – Klimisch Code 1a Note: the various K_{ow} values reflect the components in the mixture and not the mixture *per se.*
References	Dybdahl, H.P. 1993. Determination of log P_{ow} for single components in distilled tall oil. GLP Study No. 408335/475. Water Quality Institute, Horsholm, Denmark.

PHYSICO-CHEMICAL PROPERTY – OCTANOL/WATER PARTITION COEFFICIENT	
Test Substance	
Chemical Name	Tall oil pitch
CAS #	8016-81-7
Remarks	This substance is referred to as tall oil pitch in the test plan for tall oil and related substances.
Method	
Method/Guideline followed	Testing was conducted according to OECD Test Method 117, "Partition Coefficient (n-Octanol/Water) High Performance Liquid Chromatograph (HPLC) Method"
Test Type	Partition coefficient
GLP (Y/N)	Y
Year (Study Performed)	1993
Test conditions	Tall oil pitch was dissolved in methanol and the solution was analyzed by HPLC with UV detection using a mobile phase of methanol:buffer (3:1) at pH 2 and pH 7.5. As a reference substance, a mixture of seven materials was used.
Results	At pH 2, the log P_{ow} [K_{ow}] values of three components in tall oil pitch were 4.3, 6.0, and 6.9. At pH 7.5, the log P_{ow} values of three components in tall oil pitch were 2.8, 3.6, and 4.4.
Data Quality	Reliable without restrictions – Klimisch Code 1a Note: the various K_{ow} values reflect the components in the mixture and not the mixture *per se.*
References	Dybdahl, H.P. 1993. Determination of log P_{ow} for single components in tall oil pitch. GLP Study No. 408335/473. Water Quality Institute, Horsholm, Denmark.

ENVIRONMENTAL FATE – BIODEGRADATION	
Test Substance	
Chemical Name	Tall oil
CAS #	8002-26-4
Remarks	This substance is referred to as tall oil in the test plan for tall oil and related substances.
Method	
Method/Guideline followed	Testing was conducted according to OECD Test Method 301 D, "Ready Biodegradability: Closed Bottle Test"
Test Type (aerobic/anaerobic)	Aerobic
GLP (Y/N)	Y
Year (Study Performed)	1993
Contact time	28 days
Inoculum	Secondary effluent from Rungsted Treatment plant
Test conditions	Inoculum: Secondary effluent was collected from Rungsted Treatment plant in Horsholm. Concentration of test chemical: A stock solution of the test material (2 g/L) was prepared in demineralized water by ultra sonication for 5 minutes. After determination of the chemical oxygen demand, the solution was used within the same day. Test Setup: Test medium was prepared by adding 1 mL each of four solutions (potassium phosphate, magnesium sulfate, calcium chloride, ferric chloride) to 1 liter of demineralized water, which was aerated to an initial oxygen concentration of approximately 9 mg O_2/L and inoculated with 1 drop of secondary effluent per liter. The test article was added at 1.96 mg/L to a part of the inoculated test medium, equivalent to a chemical oxygen demand of 5.01 mg O_2/L. Sodium benzoate, the reference compound, was added at 2 mg/L to another part of the inoculated medium (to assess the activity of the inoculum), equivalent to a theoretical oxygen demand of 3.34 mg O_2/L. Both the test and reference articles (1.96 mg/L and 2 mg/L) were added to a third part of the inoculated medium (to assess possible inhibitory effects of the test article), at a theoretical oxygen demand of 8.35 mg O_2/L. Blank controls were prepared using the inoculated medium without test or reference materials. After the samples were prepared, the medium was transferred to calibrated respirometric bottles (BOD bottles), and placed in the dark at 20°C. The study was performed in triplicate. Sampling frequency: Samples were collected for BOD analysis on days 0, 7, 14, 21, and 28.

	Controls: Yes. Method of calculating oxygen demand: Oxygen demand was calculated as the difference between the measured oxygen concentrations at time t and the start of the test. Biological oxygen demand for the added carbon sources was calculated by subtracting the oxygen demand for the blank controls from the oxygen demand in the bottles containing test and reference compounds.
Results	
Degradation % after time	43% after 7 days and 60% after 28 days (test article); 63% after 7 days and 77% after 28 days (sodium benzoate)
Conclusions	The biological oxygen demand for tall oil was 43 and 60% of the theoretical oxygen demand after 7 and 28 days, respectively. These data indicate that the material is dominated by readily biodegradable compounds. Tall oil did not inhibit the respiratory activity of the inoculum. The inoculum had satisfactory activity as demonstrated by more than 60% degradation within the 7 days using the reference compound.
Data Quality	Reliable without restrictions– Klimisch Code 1a
References	Madsen, T. 1993. Biodegradation of distilled tall oil. GLP Study No. 308067/475. Water Quality Institute, Horshplm, Denmark.

ENVIRONMENTAL FATE – BIODEGRADATION	
Test Substance	
Chemical Name	Tall oil
CAS #	8002-26-4
Remarks	This substance is referred to as tall oil in the test plan for tall oil and related substances.
Method	
Method/Guideline followed	Testing was conducted according to OECD Test Method 301 F, Manometric respiratory test for biological degradation
Test Type (aerobic/anaerobic)	Aerobic
GLP (Y/N)	Y
Year (Study Performed)	1999
Contact time	28 days
Inoculum	Activated sludge from a municipal sewage treatment plant
Test conditions	Inoculum: Activated sludge from the municipal sewage treatment plant in Reutlingen was washed twice with dechlorinated tap water and centrifuged at 3000 rpm for one minute. Concentration of test chemical: A stock solution of the test material (102.2 mg/L) was prepared. Test Setup: Mineral medium was prepared by adding 10 mL of a potassium phosphate solution and 1 mL each of three other solutions (magnesium sulfate, calcium chloride, ferric chloride) to make a total volume of 1 liter in deionized water. Six flasks were prepared: two of the test article in mineral medium with inoculum (24 mg/L); two of the mineral medium plus the inoculum (24 mg/L); one of the reference substance [sodium benzoate (98.5 mg/L)] with inoculum (24 mg/L); and one of the test article in water with sterilized medium. Sampling frequency: Samples were collected for analysis on days 14 and 28. Controls: Yes. Method of calculating oxygen demand: Biological oxygen demand was calculated by subtracting the oxygen demand for the blank controls from the oxygen demand in the flasks containing test and reference compounds.
Results	
Degradation % after time	73% after 28 days (test article); 97% after 28 days (sodium benzoate)

Conclusions	Seventy-three percent of tall oil was biodegraded after 28 days indicating that the organic portion of the test material was inherently biodegradable.
Data Quality	Reliable without restrictions– Klimisch Code 1a
References	Aniol. S. 1999. Biological degradation, manometric respirometry test. STZ Project No. 04/99. Steinbeis-Transferzentrum Angewandte und Umwelt-Chemie, Reutungen.

ENVIRONMENTAL FATE – BIODEGRADATION	
Test Substance	
Chemical Name	Tall oil pitch
CAS #	8016-81-7
Remarks	This substance is referred to as tall oil pitch in the test plan for tall oil and related substances.
Method	
Method/Guideline followed	Testing was conducted according to OECD Test Method 301 D, "Ready Biodegradability: Closed Bottle Test"
Test Type (aerobic/anaerobic)	Aerobic
GLP (Y/N)	Y
Year (Study Performed)	1993
Contact time	28 days
Inoculum	Secondary effluent from Rungsted Treatment plant
Test conditions	Inoculum: Secondary effluent was collected from Rungsted Treatment plant in Horsholm. Concentration of test chemical: A stock solution of the test material (2 g/L) was prepared in demineralized water by ultra sonication for 5 minutes followed by magnetic stirring for 24 hours at 20°C. The solution was filtered and, after determination of the chemical oxygen demand, the solution was used within one day. Test Setup: Test medium was prepared by adding 1 mL each of four solutions (potassium phosphate, magnesium sulfate, calcium chloride, ferric chloride) to 1 liter of demineralized water, which was aerated to an initial oxygen concentration of approximately 9 mg O_2/L and inoculated with 1 drop of secondary effluent per liter. The test article was added at 186 mg/L to a part of the inoculated test medium, equivalent to a chemical oxygen demand of 4.56 mg O_2/L. Sodium benzoate, the reference compound, was added at 2 mg/L to another part of the inoculated medium (to assess the activity of the inoculum), equivalent to a theoretical oxygen demand of 3.34 mg O_2/L. Both the test and reference articles (186 mg/L and 2 mg/L) were added to a third part of the inoculated medium (to assess possible inhibitory effects of the test article), at a theoretical oxygen demand of 7.90 mg O_2/L. Blank controls were prepared using the inoculated medium without test or reference materials. After the samples were prepared, the medium was transferred to calibrated respirometric bottles (BOD bottles), and placed in the dark at 20°C. The study was performed in triplicate. <u>Sampling frequency</u>: Samples were collected for BOD

	analysis on days 0, 7, 14, 21, and 28. Controls: Yes. Method of calculating oxygen demand: Oxygen demand was calculated as the difference between the measured oxygen concentrations at time t and the start of the test. Biological oxygen demand for the added carbon sources was calculated by subtracting the oxygen demand for the blank controls from the oxygen demand in the bottles containing test and reference compounds.
Results	
Degradation % after time	36% after 7 days and 41% after 28 days (test article); 72% after 7 days and 94% after 28 days (sodium benzoate)
Conclusions	The biological oxygen demand for tall oil pitch was 41% of the theoretical oxygen demand after 7 days and did not increase during the 28 days of the experiment. These data indicate that the material contains readily biodegradable and recalcitrant compounds. Tall oil pitch did not inhibit the respiratory activity of the inoculum. The inoculum had satisfactory activity as demonstrated by more than 70% degradation within the 7 days using the reference compound.
Data Quality	Reliable without restrictions– Klimisch Code 1a
References	Madsen, T. 1993. Biodegradation of tall oil pitch. GLP Study No. 308067/473. Water Quality Institute, Horshplm, Denmark.

ACUTE TOXICITY – ORAL	
Test substance	
Chemical Name	Tall oil
CAS #	8002-26-4
Remarks	This substance is referred to as tall oil in the test plan for tall oil and related substances.
Method	
Method/Guideline followed	Test procedure was similar to OECD Test Method 401, "Acute Oral Toxicity"
GLP (Y/N)	N
Year (Study Performed)	1986
Species	Rat
Strain	Sprague-Dawley
Route of administration	Oral
Dose levels	5000 mg/kg
Sex and number/group	5 male and 5 female rats
Frequency of treatment	Single oral gavage
Duration of test	14 day observation post-treatment
Control group (Y/N)	N
Result	
Acute Oral LD_{50}	>5000 mg/kg
Detailed Summary	Crude tall oil (CAS #8002-26-4) was administered orally (via gavage) to Sprague-Dawley rats (n = 5/sex/study) at 5000 mg/kg and the animals were observed for 14 days. The study was performed two times. Parameters evaluated included mortality, clinical signs, body weight gain, and gross pathology. In the first test, one male died on day 1 and a second male died on day 7. For the females, one death occurred on day 1 and a second on day 3. The overall mortality was 40%. No body weight effects were noted. Animals surviving the treatment appeared normal and exhibited no effects at gross pathological examination. In comparison, rats dying on study exhibited erosion of the stomach epithelium and hyperemia of the intestinal tract. When the study was repeated using the same dose level, no deaths occurred, the rats appeared normal throughout, no body weight effects occurred, and there were no gross pathological findings. Based on these data, the oral LD_{50} was greater than 5000 mg/kg.
Data Quality	Valid without restriction – Klimisch Code 1b
Reference	Prince, H.N. 1986. Acute toxicity report: oral toxicity. Report No. GBL 30373. Gibraltar Biological Laboratories, Inc., Fairfield, New Jersey.

ACUTE TOXICITY – ORAL	
Test substance	
Chemical Name	Tall oil
CAS #	8002-26-4
Remarks	This substance is referred to as tall oil in the test plan for tall oil and related substances.
Method	
Method/Guideline followed	Test procedure was similar to OECD Test Method 401, "Acute Oral Toxicity"
GLP (Y/N)	N
Year (Study Performed)	1986
Species	Rat
Strain	Sprague-Dawley
Route of administration	Oral
Dose levels	6000 mg/kg
Sex and number/group	5 male and 5 female rats
Frequency of treatment	Single oral gavage
Duration of test	14 day observation post-treatment
Control group (Y/N)	N
Result	
Acute Oral LD_{50}	>6000 mg/kg
Detailed Summary	Crude tall oil (CAS #8002-26-4) was administered orally (via gavage) to Sprague-Dawley rats (n = 5/sex) at 6000 mg/kg and the animals were observed for 14 days. Parameters evaluated included mortality, clinical signs, body weight gain, and gross pathology. One female rat died on day 3; no other deaths occurred. All surviving animals appeared normal throughout the course of the study, and no body weight changes were observed. At gross pathology, no abnormalities were reported in the surviving animals; data for the animal dying on study were not presented. The oral LD_{50} was greater than 6000 mg/kg.
Data Quality	Valid without restriction – Klimisch Code 1b
Reference	Prince, H.N. 1986. Acute toxicity report: oral toxicity. Report No. GBL 30371. Gibraltar Biological Laboratories, Inc., Fairfield, New Jersey.